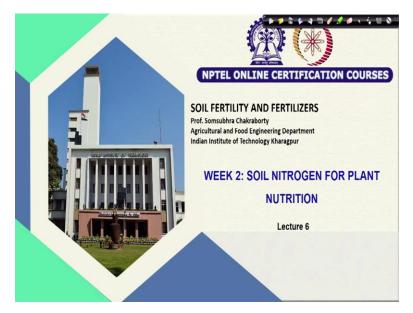
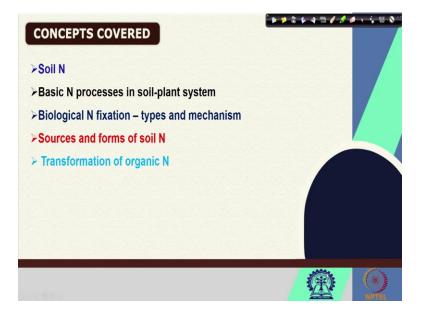
Soil Fertility and Fertilizers Professor Somsubhra Chakraborty Agriculture and Food Engineering Department Indian Institute of Technology, Kharagpur Lecture 06 Soil Nitrogen for Plant Nutrition

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Welcome friends to this second week of lectures of this NPTEL online certification course of Soil Fertility and Fertilizers. And in this week two we are going to discuss Soil Nitrogen for Plant Nutrition. Now, in this week we are going to discuss in details about the importance of nitrogen for soil plant nutrition, for plant nutrition.

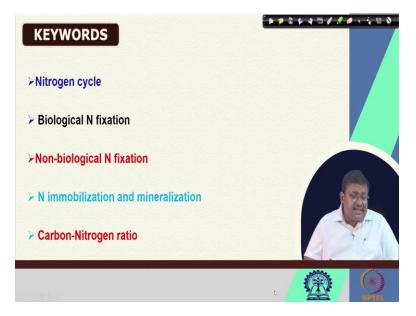
As well as we are going to discuss what are the different processes, which are related to nitrogen in the soil, which governs the availability of different nutrients for plants. So, today we are going to start Lecture 6. (Refer Slide Time: 01:01)



And in this Lecture 6 we are going to cover these following concepts. So, first we are going to discuss about soil nitrogen and then we are going to discuss about basics nitrogen processes in soil and plant system, then we are going to discuss biological nitrogen fixation there types and mechanism and then we are going to discuss sources and forms of soil nitrogen and finally, we are going to discuss the transformation of organic nitrogen.

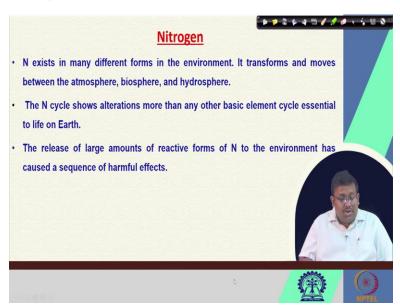
So, all of these are very important specifically the processes which we are going to discuss as well as biological nitrogen fixation, they are very much important for governing the nitrogen and their different species and their concentration in the soil plant system.

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So, these are the some of the keywords of this lecture nitrogen cycle, biological nitrogen fixation, non biological nitrogen fixation, then nitrogen immobilization and mineralization and finally, CN ratio or carbon nitrogen ratio.

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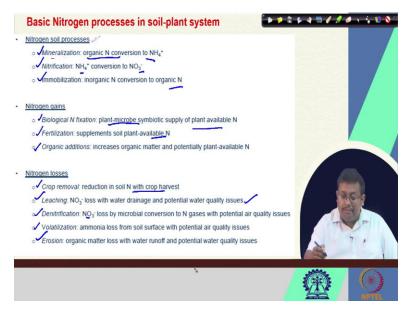


So, let us start with the basic overview of nitrogen. Now, you know that in soil nitrogen exists in many different forms, also in the whole environment it appears in different forms. So, it transforms and moves between the atmosphere, biosphere and hydrosphere. So, the nitrogen cycle shows alterations more than any other basic elemental cycle essential to life on Earth.

So, all the cycles of basic elements which are required for sustaining the life on the Earth among them nitrogen cycle is characterized by several mechanisms and several types of alterations or changes. And remember that the release of large amount of reactive forms of nitrogen into the environment has caused a sequence of harmful effects.

So, that is why it is very important to have a clear understanding of the nitrogen cycle and the different factors which influence the concentration of different nitrogen species in the soil, so that we can minimize these harmful effects from the excessive amount of some nitrogen species.

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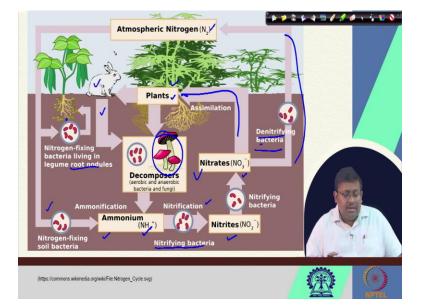


So, if we go ahead and see what are the basic nitrogen process in soil plant system, you know these are, we have listed these here. So, basic nitrogen soil process you can see these are mineralization, let me just make this little. Now, the first important process is mineralization, which is basically conversion of organic nitrogen to ammonium. The second one is nitrification which is conversion of ammonium ions to nitrate and then finally immobilization which is inorganic nitrogen conversion to organic nitrogen.

So, these are major nitrogen related soil process. Now, what are the gains of nitrogen? The first important source of nitrogen here it is biological nitrogen fixation which basically comes from plant microbe symbiotic relationship and that supply the plant available nitrogen. Secondly, another source of nitrogen is fertilizers. So, when you go for fertilization that supplement soil plant available nitrogen. The third one is organic additions.

So, when we apply these organic matter in the soil that enhances the potentially plant available nitrogen in the soil. So, these are the pathways through which nitrogen is augmented in the soil. The processes through which nitrogen get lost from the soil are, first of all is the crop removal which is the reduction in soil nitrogen with crop harvest. Second one is leaching which is basically, the leaching of nitrogen basically occurs for nitrate species, so generally nitrate loss with water drainage and potential water quality issues, this is the leaching process.

Another process is called denitrification process where nitrogen nitrate is lost by microbial conversion to nitrogen gases with potential air quality issues. And fourth one is volatilization and where ammonia is loss from soil surface and creating different types of potential air quality issues. And finally, erosion, erosion is organic, loss of organic matter with water runoff and potential water quality issues. So, these are the pathways through which nitrogen is lost from the environment.



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So, this is an overview of the nitrogen cycle. We will discuss this cycle in details in our upcoming slides, but just to have an idea about what actually goes on in the soil, so, let us start with the atmosphere nitrogen which is dinitrogen gas. So, from this atmosphere nitrogen different types of nitrogen fixing bacteria, which are there in the soil, they are of two types one is freely non symbiotic nitrogen fixing bacteria and other is symbiotic nitrogen fixing bacteria.

Symbiotic nitrogen fixing bacteria generally resides in the root nodules of some leguminous plants and non symbiotic nitrogen fixing bacteria are present in the soil. So, these two groups of microbes basically fix this atmospheric nitrogen and this atmospheric nitrogen is taken up by these, they are being fixed by these microbes and these nitrogen is been taken up by the plants. So, here you can see this nitrogen fixing bacteria living in legume root nodules and also there are some nitrogen fixing freely, the free living soil bacteria.

So, ultimately these bacteria helps in ammonification process which is conversion of, which is basically release of ammonium ions, from these ammonium ions nitrification process starts in the presence of nitrifying bacteria ultimately produces nitrites and then in the second step it produced the nitrates So, these nitrate is being assimilated by the plant. So, plant can assimilates these nitrates and after the death of these plants and plants, from the plants different types of animals can get their food.

So, after the death of both plants and animals, there are decomposers present in the soil they decompose the plant body as well as the animal body. So, basically there these decomposers are aerobic and anaerobic bacteria in fungi and they ultimately helps in increasing the ammonium concentration in the soil through ammonification process.

So, we are going to discuss those steps if in details, but at the same time you should remember that these nitrates one part of these nitrate is also converts back to these atmospheric nitrogen by the denitrification process and this is mediated by denitrifying bacteria. So, this is how these nitrogen moves from air to soil and again back from soil to atmosphere. So, this is how, this is an overview of nitrogen cycle, of course, we are going to discuss this nitrogen cycle in details in our upcoming slides.

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► # \$ + 4 = 1 # # + 1 = 0
Biological N fixation
Symbiotic N fixation:
➤ Mediated by bacteria with the ability to convert atmospheric N ₂ to plant-
available N while growing in association with a host plant.
➤ Example: Rhizobium bacteria fix N₂ in nodules present on the roots of legumes
such as soybeans.
Non-symbiotic N fixation
> N ₂ fixation process that is performed by free-living bacteria in the soil.
Amount of N fixed by these organisms is much lower than that fixed by
symbiotic N fixation.

Now, what is biological nitrogen fixation? Now, biological nitrogen fixation I told you that it is basically fixing of atmospheric nitrogen by the microbes which are present in the soil, they are either present freely in the soil or they are present in the root nodules of some leguminous plants. So, they are of two types one is symbiotic nitrogen fixation and other is non symbiotic nitrogen fixation.

Now, this symbiotic nitrogen fixation is basically mediated by bacteria with the ability to convert this atmospheric nitrogen gas to plant available nitrogen while growing in association with the host plant. So, there is always some symbiotic relationship between certain species of Rhizobium bacteria and specific Leguminosae plant. So, in this symbiotic relationship this nitrogen fixing bacteria basically converts this atmospheric nitrogen into available nitrogen and these available nitrogen is being used by the host plant.

For example, Rhizobium bacteria fix nitrogen in nodules present in the roots of legumes such as soybeans. The other type of biological nitrogen fixation is non symbiotic nitrogen fixation. Now, in this process, nitrogen fixation is performed by free living bacteria in the soil and the amount of nitrogen fixed by these organisms is much lower than that fixed by symbiotic nitrogen fixation. So, obviously, symbiotic nitrogen fixation is having more importance than non symbiotic nitrogen fixation.

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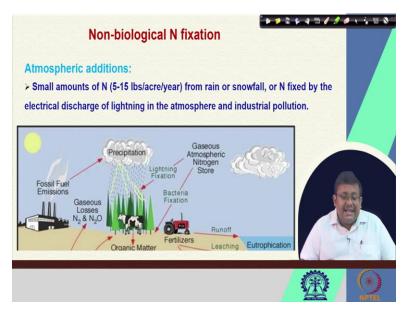
1 1 1 1 1 Biological nitrogen fixation (BNF) occurs when atmospheric nitrogen is converted to ammonia by a nitrogenase enzyme. The overall reaction for BNF is: $+16 \text{ ATP} + 16 \text{ H}_{\circ} \text{O} + 8 \text{ e}^{-} + 8 \text{ H}^{+}$ > The conversion of N2 into ammonia occurs at a metal cluster called FeMoco, the iron molybdenum cofactor. The mechanism proceeds via a series of protonation and reduction steps wherein the FeMoco active site hydrogenates the N2 substrate.

Now, the biological nitrogen fixation we sometimes call it a BNF in short form occurs when atmospheric nitrogen is converted to ammonia by an enzyme. So, an enzyme plays a important role in this biological nitrogen fixation that is called Nitrogenase enzyme. So, if we see the overall reaction of this biological nitrogen fixation

So, we can see we are starting with the dinitrogen gas then we are using this, this process use 16 ATPs then water and then electrons and protons and ultimately creating these ammonia gas and then hydrogen gas and also ADP plus Pi. So, we can see the conversion of nitrogen into ammonia and these conversion of nitrogen into ammonia occurs as a metal cluster which is called F E M O C O or FeMoco which is also basically the iron molybdenum cofactor, Fe stands for iron, molybdenum Mo and cofactor stands for co.

So, FeMoco is basically iron molybdenum cofactor and these mechanism proceeds via a series of protonation and reduction steps where in DC for this FeMoco active side hydrogenates dinotrogen gas substrate. So, basically the idea is it is these dinotrogen gas is hydrogenated to form these ammonium, this ammonia and so, so, this is basically mediated by these iron molybdenum cofactor with the presence of Nitrogenase enzyme.

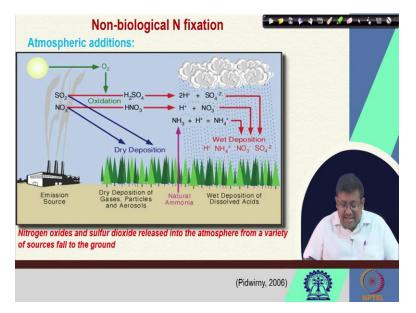
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So, now, let us see the non biological nitrogen fixation. We have seen the biological nitrogen fixing what are the non biological nitrogen fixation. Now, atmospheric addiction is an example of non biological nitrogen fixation. For example, there are different types of fossil fuel emission, from the fossil fuel emission different gases are produced like nitrogen oxides and different oxides of nitrogen and sulfur and then ultimately they mixed with atmospheric water vapor and then comes back to the soil through acid rain in the form of precipitation and also there as gaseous losses of nitrogen and N2O which also create this precipitation.

And also when there is a lightning that also fix nitrogen and ultimately comes to the soil in the form of precipitation. So, there are different ways through which these nitrogen is getting fixed from atmosphere. So, small amount of nitrogen that is from 5 to 15 pound per acre per year generally comes from rain or snowfall or nitrogen fixed by the electrical discharge of lightning in the atmosphere and industrial pollution. So, these are some atmospheric, examples of atmospheric addition of nitrogen.

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So, also you can see that this is more detail. So, here due to different types of emission sources or industrial processes, this nitrogen oxides and sulfur dioxide are emitted. And they form these H2SO4 and HNO3 by reacting with different water vapor and ultimately they get deposited in the form of wet deposition. So, basically they dissociate to form sulfate, nitrate and these ammonia also.

So, the sulfate and nitrates comes back to the soil through wet deposition. Also, there are some ammonia volatilizations, so there is the ammonia goes to the atmosphere and reacts with the protons and forms this ammonium ion and that also comes back to the soil through wet deposition process. So, through wet deposition process, you can see there are H plus, ammonium, nitrate and sulfate all these important ions are coming back into the soil.

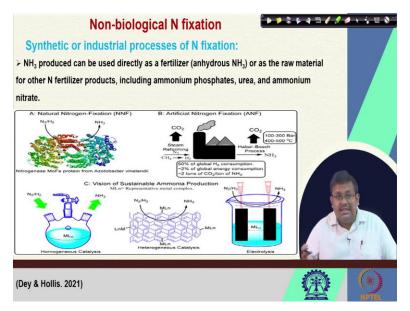
So, these are some atmospheric additions. So, at the same time, the sulfur dioxide and nitrogen oxides are also dry deposited as gases or particle or aerosols. So, these are different sources of atmospheric addition of this nitrogen. So, these nitrogen oxides and sulfur dioxide released into the atmosphere from a variety of sources and ultimately fall to the ground. So, this is an example of atmospheric, these are some examples of atmospheric additions.

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Non-biological N fixation
Synthetic or industrial processes of N fixation:
> Industrial fixation of N is the most important source of N as a plant nutrient.
> Based on the Haber-Bosch process where
hydrogen (H_2) and N_2 gases react to form NH_3 :
$N_2 + 3H_2 \longrightarrow 2NH_3$
$N_2 + 3H_2 \rightarrow 2NH_3$
THE HABER-BOSCH PROCESS

Now, if we see the synthetic or industrial process of nitrogen fixation. So, industrial fixation of nitrogen is the most important source of nitrogen as a plant nutrient and it is basically based on Haber-Bosch synthesis process. So, this in this Haber-Bosch synthesis process basically there is we generally in the near industry, hydrogen and nitrogen gas are combined through a reaction to form this ammonia. So, here you can see this is a nitrogen gas and then it reacts with these three molecules of hydrogen gas and ultimately produces two molecules of ammonia and this process is known as the Haber-Bosch process.

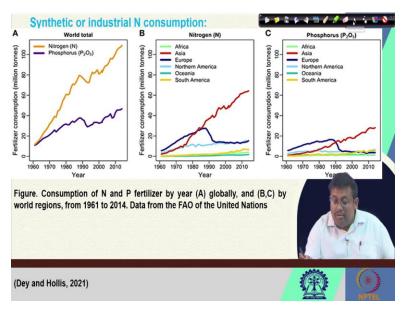
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So, this is a major process through which industrially the nitrogen is getting fixed. And also there are some synthetic and some ammonia is also produced through this Haber-Bosch process. So, we are seeing the ultimate end product is ammonia. So, this ammonia which is produced can be used directly as a fertilizer, which is also known as anhydrous ammonia or as a raw material for other nitrogen fertilizer products, for example, ammonium phosphate, urea, ammonium nitrate, so, these are all nitrogenous fertilizers.

So, for the production of these nitrogenous fertilizer we require these ammonia as a raw material. So, we can either use these ammonia gas as an anhydrous ammonia as a fertilizer itself or we can use this ammonia gas as a raw material for production of these nitrogenous fertilizers.





Now, let us see the worldwide trend of synthetic or industrial nitrogen consumption. So, in this first plot you can see this is a nitrogen fertilizer consumption trend from 1960 to 2010. And we can see also the phosphorus consumption trends also, although the nitrogen consumption is, although this nitrogen consumption rate is quite higher than that of phosphate, but we can also see the increased consumption of phosphorus.

Here, in this plot we can see that changes in nitrogen consumption in different continents. So, we can see that, in Asia, there has been a steady rise of nitrogen fertilizer consumption in million tons for last 50 to 60 years. And this could be due to the intensification of agricultural practices in Asia.

And in other continents as compared to the other continents, however, we can see there is a decline a decrease of fertilizer consumption in Europe. And in case of phosphorus also, we can see the same trend, where Asia shows the highest phosphorus consumption for last 50 to 60 years. So, that shows the importance of these fertilizers on agricultural intensification and how these consumptions have been increasing since last 60 years in different agricultural sectors.

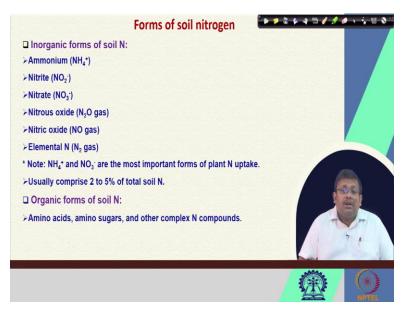
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DBT Sales of different Fertilizers during 2019-20 vis-å-vis 2018-19 (Figure in LMT) 400 350 320.4 356.97 300 250 250 250 250 250 250 250 250 250 2	2018-19 2019-20		
UREA DAP MOP NPKS	D=1640400)	b	

Now, also you can see here this is India data. So, in the Indian data you can see how these different fertilizers or the sales of different fertilizers, nitrogen and then phosphorus and potash fertilizers, how their sales have been in changed in the agenda 2019-20 as well as 2018 and 19. So, this one is 2019-20 and this is 2000, the blue bar is showing the sale in 2018-19.

So, you can see for all the fertilizers starting from Urea, DAP and NPK fertilizer except for this MOP which is more or less same. So, this Urea, DAP and NPK fertilizers are showing higher sales of these different fertilizers, during 2019 then 2018. So, that shows the continuous increase of fertilizer consumption in India also and that may be due to also agricultural intensification.

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So, what are the different forms of soil nitrogen? You can see that there are different inorganic forms of soil nitrogen like ammonium, nitrite, nitrate, then nitrous oxides, then nitric oxides or NO gas, then elemental nitrogen or nitrogen gas. Remember that among these ammonium and nitrate are the most important forms of plant nitrogen uptake, because plant can only take these two forms of nitrogen.

And remember that these organic forms of soil nitrogen whatever we have talked about these usually comprises 2 to 5 percent of the total cycle nitrogen, so that means, most of the soil nitrogen are present in organic forms. So, what are the organic forms of soil nitrogen? Amino acids, amino sugars and other complex nitrogen compounds are the examples of nitrogen compounds or organic forms of soil nitrogen.

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• • • • • • • • • • • • • • Transformation of organic Nitrogen Mineralization: > The process by which nitrogen in organic compounds gets converted into inorganic ammonium and nitrate ions. > The complex organic forms of N present in plant and animal residues are attacked by heterogeneous group of soil micro-organisms and are converted into NH4* and NO3 forms > The process comprises series of reactions brought forward by soil microbes till the formation of NO3 > The reaction is faster in the presence of substrates (carbon source)

Now, let us see what are the major process through which this organic nitrogen gets converted from one form to another form? So, the most important process is mineralization process. So, in this process basically, the nitrogen in the organic compound gets converted into inorganic ammonium and nitrate ions. And the complex organic forms of nitrogen present in plant and animal residues are attacked by different types of heterogeneous groups of soil microorganisms and then they are converted into ammonium and nitrate forms.

Remember that these ammonium and nitrate are the two important forms which plant can uptake. So, these are plant available forms. So, to become plant available, this organic form of nitrogen which accounts for 95 percent of the total soil nitrogen has to be converted into these inorganic forms before plant can uptake them. So, the process comprises series of reaction brought forward by soil microbes in the formation of nitrate. So, this is called mineralization process.

And there remember that this reaction is faster in the presence of substrate. When there is a substrate that means, organic sources, organic carbon source that basically gives them the energy, so basically this organic matter when we apply organic method that acts as a carbon source for these different microbes. And as a result, the reaction is getting faster in the presence of these different types of microbes which facilitates, which facilitate this mineralization process.

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Nitrogen Mineralization & Immobilization	**************************************
➤ N mineralization is the conversion of organic N to NH4 ⁺ .	
\succ Important process in the N cycle since it results in the	e liberation of plant-
available inorganic N forms.	
>Immobilization is the conversion of inorganic plant	
available N (NH_4^+ or NO_3^-) by soil microorganisms to organic	\frown
N forms (amino acids and proteins).	Organic N
> Reverse of mineralization, Immobilized forms of N are not	Immobilization (NH ₄ *, NO ₃ *)
readily available for plant uptake.	

Now, as we know that nitrogen mineralization is a conversion of inorganic form of nitrogen to ammonium and this is an important process in the nitrogen cycle since it results in the liberation of plant available inorganic nitrogen from. What is the opposite process? The opposite process is known as immobilization. Immobilization is just the opposite of mineralization.

So, it basically the conversion of inorganic plant available nitrogen that is ammonium and nitrate by soil microorganisms to organic nitrogen forms, what are the organic nitrogen forms, amino acids and proteins, so these two are the organic nitrogen forms. And immobilization is basically conversion of these ammonium and nitrate into these organic nitrogen forms. So, what do we understand?

We understand that the immobilization is a reverse process of mineralization and remember that these immobilized forms of nitrogen are not readily available for plant uptake because they are a amino acids and proteins and plant cannot uptake amino acids and proteins because only there are two available forms that is ammonium and nitrate which are inorganic forms.

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Now, please recall that mineralization and immobilization occurred simultaneously in soil, however, the net balance between the two varies with environmental conditions and the characteristics of the organic material available for decomposition. Now, remember that both mineralization and immobilization are accelerated by conditions favorable for microbial growth.

What are four factors? First of all moist soil, warm temperature, good aeration, easily degradable, organic substrate material, physical mixing of soil via tillage and higher soil pH, all these are very much important for mineralization process for creating favorable condition for mineralization and immobilization process.

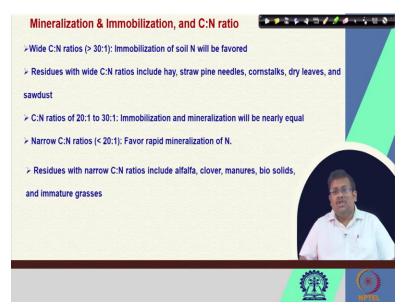
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* 🕨 📚 🖡 🖉 🗇 🖉 🏉 🗸 🐇 🖾 🛇 Mineralization & Immobilization, and C:N ratio >Immobilization and mineralization can be disrupted by the incorporation of organic residues that have high carbon to nitrogen ratios (C:N) >The ratio of % C to % N, or the C:N ratio, defines the relative quantities of these elements in residues and living tissues >Whether N is mineralized or immobilized depends on the C:N ratio of the organic matter being decomposed by soil microorganisms

Now, we have also discussed in our previous week, the importance of C:N ratio. Now, remember that and we have also discussed why C:N ratio governed this immobilization and mineralization. So, if you recall, that immobilization mineralization can be disrupted by the incorporation of organic residues that have high carbon to nitrogen ratio. So, the ratio of carbon to nitrogen that is the C:N ratio defines the relative quantities of these elements in residues and living tissues.

So, where the nitrogen is mineralized or immobilized depends on the C:N ratio of the organic matter being decomposed by soil microorganisms.

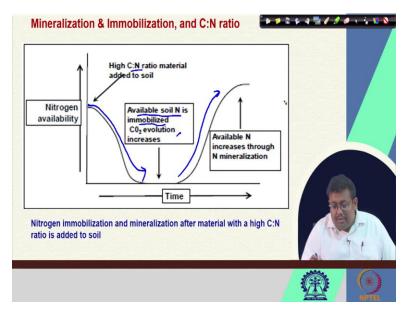
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So, we already know that when there is a wide C:N ratio that which is greater than 30 is to 1 then immobilization of soil nitrogen will be favored. And some of these types of materials which are having these wide C:N ratios are hay, straw pine needles, then cornstalks, dry leaves and sawdust these are having high C:N ratios.

So, they decompose very slowly. And C:N ratios between 20 is to 1 to 30 is to 1, and in the range, these immobilization and mineralization will be almost equal to each other. However, when the C:N ratio is less than 20 is to 1 that favores the rapid mineralization of nitrogen. So, residues of narrow C:N ratios are alfalfa, clover, manures, bio solids, and immature grasses. So, they decompose very fast.

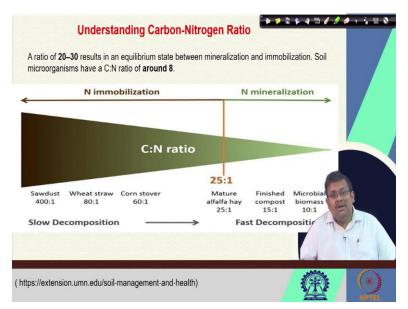
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Now, if we see the nitrogen availability as a function of time, we can see that nitrogen immobilization mineralization, the changes after we add the material with high C:N ratio in the soil. So, here you can see, when we are adding the material with high C:N ratio in the soil the nitrogen availability goes down with time because the available soil nitrogen is immobilized and the same time carbon dioxide evolution increases.

So, when the C:N ratio when we add a material with C:N ratio it will favor the immobilization, so, nitrogen availability will go down. And after a certain time again these available nitrogen content will increase through nitrogen mineralization, because when these immobilization will take place, and those plants will die after some time they will decompose and further release these nitrogen, so that available nitrogen will also increase after a certain period of time through nitrogen mineralization process. So, this is how these nitrogen availability changes when we add different residues with varying C:N ratio.

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Now, we have seen the same slide previously also, so a ratio of 20 to 30 results in an equilibrium state between mineralization and immobilization, and soil microorganisms have a C:N ratio of around 8. So, we can see a cutoff value say an approximate cutoff value of C:N ratio you can see here that is 25 is to 1 which is in between 20 to 30 and that is basically match your alfalfa, hay and also finished compost have 15 is to 1, microbial biomass has 10 is to 1, so that these helps fast decomposition.

However, sawdust, wheat straw, corn strover these are having higher C:N ratio, so they favor the nitrogen immobilization. So, this is how the C:N ratio governs this nitrogen mineralization and immobilization.

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So, guys I have completed this Lecture 6 and these are some of the references you can explore for more information regarding these nitrogen cycle. We will continue this nitrogen cycle in our upcoming lectures also, but for now, let us wrap up this lecture and let us meet in our next lecture. Thank you.